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THERMO-OXIDATIVE STABILITY OF GRAPHITE FIBER/PMR-15
POLYIMIDE COMPOSITES AT 350°C

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A series of graphite fiber/PMR-15 polyimide composites were subjected to isothermal aging at 350°C in flowing air (100 cc/min and 1000 cc/min) over a 520 hr time period. The graphite fibers were analyzed by ISS/SIMS techniques before composite fabrication. Fibers exposed at the surface of the composite due to the isothermal aging process were also analyzed by the ISS/SIMS method. Component and composite weight loss studies were also conducted for similarly exposed materials. Optical micrograph investigations of composites to follow the progress of the thermo-oxidative process were also conducted. Flexural and interlaminar shear strengths of the unaged and aged composites were measured. The relationship of component and composite properties as they relate to the thermo-oxidative behavior of the materials was discussed.

INTRODUCTION

The long term durability of graphite fiber reinforced PMR-15 polyimide composites at 316°C and above, is dependent on the two major aspects of these composite systems. These are (1) the thermal and thermo-oxidative stability of the individual components and (2) the influence of the interface region between fibers and matrix on matrix stability. In studies carried out at 316°C (600°F) on several fiber/PMR-11 and PMR-15 polyimide systems, in flowing air, it has been demonstrated that the thermo-oxidative stability of these systems is effected by fiber surface impurities, such as the alkali metal ions, sodium and potassium (ref. 1). Gibbs et al. (ref. 2) have shown that HTS graphite fibers contain a large concentration of sodium ions on the surface, while Dryzal and Hammer (ref. 3) have demonstrated that AS graphite fibers also contain large concentrations of sodium ions relative to other graphite fibers. The overall objectives of this investigation are (1) to determine the mechanism of the thermo-oxidative process in flowing air of several composite systems consisting of the addition polyimide PMR-15 in combination with the graphite fiber reinforcements, and (2) to determine the upper temperature limit of these composite systems.

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In the present paper the surface composition of several graphite fibers as determined by ISS/SIMS analysis and the relationship of the surface composition to component properties and composite thermo-oxidative stability will be discussed. Thus, the surfaces of the neat fibers and fibers from composites exposed as a result of the thermo-oxidative process were analyzed. Weight loss studies of the component materials and each graphite/PMR-15 composite system were conducted. Optical microscopy and mechanical property measurements of the "as fabricated" and isothermally exposed composites were also carried out.

EXPERIMENTAL

Fiber Materials

Fiber materials were obtained commercially; AS from Hercules Inc., Thornel 300 from Union Carbide Corp., Celion 6000 from Celanese Corp., Fortafil 5 from Great Lakes Carbon Corp., and Panex 30 from Stackpole Carbon Corp. The following fibers were investigated: Panex 30 (unsized) (Roll #18-00506), Fortafil 5 (unsized) (Lot #SeRS-1528-B), Fortafil 5 (P.I. compatible size, not PI) (Lot #2237-29-15), Celanese 6000 (unsized) (Lot #HTA-7-8422), Celanese 6000 (NR150B2 size) (Lot #HTA-7-9821), Thornel 300 (water sized) WYP 30 1/0, AS4W6 (water size) (Lot #205-1), and Celion 6000 (Celanese PI size) (Lot #HTA-7-2832).

PMR-15 Polyimide Resin

The polyimide resin system used in this study was prepared and processed from a methanol solution of monomers as described previously (refs. 4,5).

ISS/SIMS Analysis of Fiber Surfaces

The equipment and procedures used in the surface analysis by Ion Scattering Spectroscopy (ISS) and Secondary Ion Mass Spectroscopy (SIMS) have been described previously (ref. 6). Table 1 lists the conditions for the analysis. For the ISS analysis, samples were bombarded by a primary ion beam of $^3\text{He}^+$ at an energy of 2.5 keV and a beam current density of $1.3\mu\text{amps}/\text{cm}^2$. For the SIMS analysis, samples were bombarded by a primary ion beam of $^{20}\text{Ne}^+$ for a near surface analysis (5-10Å) and again at the approximate sputtered depth of 100Å, at a beam energy of 2.5 keV and a beam current density of $1.3\mu\text{amps}/\text{cm}^2$. Surfaces were sputtered using a Perkin Elmer PHI sputter ion gun at a beam energy of 5 keV and a current density of $14.3\mu\text{amps}/\text{cm}^2$. The sputter rate was approximately $5\text{Å}/\text{min}$. The SIMS data for each fiber are reported in relative atomic ratios. These were calculated as follows: the values of counts per second (c/s) of each element on the fiber surface were adjusted to relative atomic values by dividing each c/s value by the sensitivity factor for that element. These relative atomic values were then normalized by dividing the relative atomic value of each element on a given fiber surface by the relative atomic value of

each element on a given fiber surface by the relative atomic value of the element present in the smallest amount. For the data at the 5-10Å level, hydrogen atomic ratios were calculated but not reported since the hydrogen ratios are high for all fibers, as expected. In addition, since high levels of C^+ , CH^+ , CH_2^+ , CH_3^+ and C_2H^+ species were observed in most fibers, these were not considered in the atomic ratio calculation. Moreover for species other than ^{12}C , correction factors do not exist. The data can be considered as relative atomic ratios of elements on a carbonaceous substrate.

To compare the elemental surface compositions between fibers, the relative atomic values for each element determined as described above were divided by the smallest relative atomic value observed for that element in the series of fibers analyzed. Such comparisons assume that substrate effects on the sputtering of easily ionized elements are negligible.

PMR-15 composites of each fiber were fabricated and subjected to isothermal aging at 350°C in flowing air, 100 cc/min or 1000 cc/min for time periods up to 700 hrs. The surfaces of the fibers, exposed as a result of this thermo-oxidative process, were also examined by the ISS/SIMS technique.

Isothermal Weight Loss Measurements

Fibers, neat PMR-15 resin and composites were weighed at various time periods to determine weight changes due to the 350°C, air flow (100 cc/min or 1000 cc/min) exposure.

Isothermal Aging Procedure

Component materials and precut flexural and interlaminar shear composite specimens were placed in the center 20 cm portion of a ceramic tube 5.0 cm diameter x 61 cm in length. A constant temperature of 350°C was maintained in the 20 cm zone area where the specimens were being aged. Air was passed into the tube at a rate of 100 cc/min or 1000 cc/min depending on the study.

Composite Fabrication

Graphite fiber/PMR-15 composites were fabricated from PMR-15 impregnated fiber tape. The tape was prepared by brush coating a 50 wt% of PMR-15 resin components in methanol onto a dry wound tape 11.3 cm (4.5") wide x 43.2 cm (17") in diameter. The impregnated tape was cut into the appropriate lengths, 25.4 cm (~10"), then 19 layers were stacked one over the other in a mold. The mold was subjected to a heat treatment at 200°C for 1 hour to form an imide prepolymer. The female portion was positioned into the mold and the assembly was placed in a preheated press (232°C). Pressure (6.9 MPa, 1000 psi) was applied immediately to consolidate the layers, released at 232°C, then reapplied. The temperature was raised to 316°C, and the system

was maintained at these conditions (316°C, 6.9 MPa, 1000 psi) for 1 hour. The composite was cooled to RT under pressure and postcured in air in the free state by a graduated increase in temperature to 316°C over an 8 hour period, followed by a hold at this temperature for 12 hours.

The nominal dimensions of each composite were 11.4 cm x 25.4 cm x 0.254 cm (4.5" x 10" x 0.10"). Interlaminar shear specimens 0.64 cm wide x (4 x thickness + 0.25 cm) and flexure specimens (0.64 cm wide x (20 x thickness + 0.25 cm)) were cut from each composite for mechanical tests and isothermal aging studies.

Mechanical Property Measurements

Flexural strength measurements were made by the 3 point bend method at a span-to-depth ratio of 20/1 (ASTM-D-790) and crosshead speed of 0.127 cm/min (0.05 in/min). The interlaminar shear strength measurements were made by the 3 point bend method at a span-to-depth ratio of 4/1 and crosshead speed of 0.127 cm/min (0.05 in/min) (ASTM D-2344).

RESULTS AND DISCUSSION

ISS/SIMS Analysis of Fibers

Typical ISS spectra are shown in Figs. 1b, 2b and 3b. ISS spectra for the other samples are not shown. All samples reveal the presence of carbon, oxygen, sodium, and potassium within 5-10Å of the surface. In addition to these elements, unsized Fortafil 5 shows a high concentration of chromium (Fig. 1b) whereas the sized Fortafil 5 fiber shows the complete absence of the chromium ion (Fig. 2b). Celion 6000 NR-150B2 sized shows a high concentration of fluorine (Fig. 3b) as expected since the NR-150B size is a fluorinated material. The high chromium and fluorine levels for these fibers are also revealed in the SIMS spectra (Figs. 1a and 2a). Data from the ISS analysis were not used semi-quantitatively in this study, but were used to corroborate the SIMS results.

The relative atomic ratios of the elements present on the fiber surfaces at near surface (5-10Å) and after sputtering to a depth of ~100Å are listed in Tables 2 and 3. Typical SIMS spectra are shown in Figs. 1a, 2a and 3a. It should be mentioned that all fiber surfaces at 5-10Å show the presence of organic species, based on masses corresponding to C⁺, CH⁺, CH₂⁺, CH₃⁺, C₂⁺ and C₂H⁺ which sputtered from the surface. In addition, all show a high concentration of hydrogen which is a reflection of the presence of hydrocarbons, water, and hydrogen-containing graphite fibers. The carbon and hydrogen concentrations were not considered in the calculation of atomic ratios for the 5-10 and ~100Å levels. The ions of special interest at both the 5-10Å and 100Å levels are sodium, potassium, calcium, chromium and iron. At the 5-10Å level (Table 2), sodium is present at a very high concentration on the Panex 30 (unsized) fibers, (relative atomic ratio 110), and on the unsized Celion 6000,

Thorne1 300, and AS graphite fibers at relative atomic ratios of 8.4, 3.1 and 2.8 respectively. The potassium concentrations on all fibers are lower than the sodium concentrations and much lower than the iron concentrations, except for AS fibers, which do not contain iron. A high chromium concentration is noted for unsized Fortafil 5, Panex 30 (unsized) and Celion 6000 unsized and PI sized. The ISS spectrum (Fig. 1b) for Fortafil (unsized) also shows the presence of chromium. Except for Magnamite AS4(u) fibers, all fibers contained considerable quantities of iron. The presence of fluorine on AS4(u) is noted. This element is also present at the 100Å level. The high concentration of calcium on unsized and PI sized Celion 6000 is also noted. This element persists at the ~100Å level, but at much lower concentrations.

At the ~100Å level (Table 3), all but Panex 30(u) and Fortafil 5(u) contain calcium. AS4(u) is the only fiber which shows the presence of fluorine. It should be noted that there is a significant reduction of the sodium content at the ~100Å level (Table 3) on all fiber surfaces, except for AS4(u) where an approximate two-fold increase is found. Iron persists in all fibers at approximately one-third to one-quarter the levels exhibited at the ~10Å level. Chromium is now detected on Thorne1 300(u), AS4(u) and Celion 6000 PI size, whereas this element was not detected at the 10Å level in these fibers.

In comparing elements present on each fiber surface from fiber to fiber, the relative atomic ratios based on counts/sec of a given element were calculated as described in the experimental section. The results are listed in Tables 4 and 5 for near surface ~10Å and ~100Å depths respectively. At the ~10Å level, a high relative atomic ratio of sodium is noted on Panex 30(u) and Celion 6000(u); a high atomic ratio of calcium is also noted for Celion 6000(u). The potassium atomic ratio for Celion 6000 PI size is high relative to the other fibers. The high atomic ratio of chromium on Fortafil 5(u) and Panex 30(u) should be recognized. With these exceptions, the relative atomic ratio of elements listed are essentially equivalent. At the 100Å depth (Table 5), two fibers, Panex 30(u) and AS4(u), show very high relative atomic ratios of sodium compared to the other fibers. Moreover, AS4 fiber also contains a very high level of potassium, calcium, chromium and iron relative to the other fibers. The high relative atomic ratio of calcium on Celion 6000 unsized and sized is also apparent. With these exceptions the levels of elements present on the surface in comparing fiber to fiber are essentially equivalent.

ISS/SIMS Analysis of Fibers from Isothermally Aged Graphite Fiber/PMR-15 Composites

Exposure of the graphite fiber/PMR-15 polyimide composite to flowing air (100 cc/min) or (1000 cc/min) at 350°C for time periods of 250 hrs or longer caused surface oxidation of the polyimide resin, thereby exposing graphite fibers on the periphery of the composite in the process. The exposed fibers were then analyzed by the ISS/SIMS technique in the same manner as described for the neat fibers. Composite samples from each series were handled with care in order to prevent contamination of the fiber on the top surface of each sample.

Examples of ISS spectra of fibers from two isothermally aged composites, Celion 6000(u)/PMR-15 and Panex 30(u)/PMR-15 are shown in Fig. 4. Of significance in these spectra is the large peak (counts/sec) due to sodium on the Panex 30(u) fiber relative to the Celion 6000(u) fiber. A high concentration of sodium was also found in Panex 30 fibers before composite fabrication. Examples of SIMS spectra of fibers from Celion 6000(u)/T300(u)/AS4(u) composites at the 10Å level are shown in Fig. 5. The high counts/sec of sodium on T300(u) and AS4(u) relative to Celion 6000(u) and Fortafil 5(u) should be noted. The ISS/SIMS analyses were conducted after 250 hrs at 350°C in an air flow of 1000 cc/min. The relative atomic ratios of elements present on each fiber surface are compared at two depths of penetration, near surface ~10Å and at ~100Å and are listed in Tables 6 and 7 respectively. For an appreciation of the actual atomic counts/sec which these numbers represent, the actual counts/sec for each specific element, for example sodium, present in the lowest atomic count/sec from fiber-to-fiber is given as a footnote to the tables. Therefore, it can be seen that a high value for a relative atomic ratio for a specific element does not necessarily mean that the fiber or composite contains a high concentration of that element on the surface. However, it is clear that at near surface ~10Å and at ~100Å, sodium is by far the element present in the greatest concentration; approximately 5 times potassium, 30-60 times calcium, 200-800 times chromium, 200-400 times iron. Fluorine was found to be present in only AS4(u) fiber.

The relative atomic ratios of sodium for each fiber and composite material are compared in Table 8. Of particular interest is the significant change in sodium concentration from the near surface ~10Å, to the 100Å level in the AS4(u) neat fiber and in the Panex 30(u) fiber from the composite. Also, the higher concentration of sodium is noted on the T300(u), and Fortafil 5(u) fibers from the composite than was observed on the neat fiber at the 10Å and 100Å levels.

Optical Micrographs of Unaged and Isothermally Aged Composites

Optical micrographs of cross sections, transverse to the fiber direction, of the "as fabricated" isothermally aged composites after 250 and 520 hrs at 350°C in flowing air (1000 cc/min) are shown in Figs. 6 through 11. With the exception of the Fortafil 5(u)/PMR-15 composite, each composite after 250 hrs exposure developed surface cracks on the ends of the composite. Furthermore, oxidation of the surface resin on the periphery of each composite generates a covering of loose fibers. The cracks are not apparent after the 520 hr exposure, but considerably more surface fibers appear. This is true for all composites, with the extent of the cracking and quantity of surface fibers dependent on the graphite fiber/PMR-15 composite system.

Component and Composite Weight Loss

The fiber, resin and composite weight losses after exposure at 350°C in an air flow (1000 cc/min) for several hours are listed in Table 9. Composite weight losses

at 350°C in an air flow of 100 cc/min were almost identical to the 1000 cc/min air flow weight losses. The component and composite weight losses over approximately 700 hrs are shown graphically in Figs. 12 and 13. The high weight loss (78%) of the PMR-15 neat resin after 385 hrs is particularly revealing since several of the composites show very low weight loss after 520 hrs. This suggests that after the surface polyimide resin is oxidized, the fiber forms a protective blanket over the composite, acting as a scavenger for the oxygen present. The formation of a passive layer on the resin from components of the fiber thereby inhibiting oxidation of the matrix is also a possibility. The poor thermo-oxidative stability of the Thornel 300(u) and Panex 30(u) relative to the other fiber is also noted. Moreover, the poor thermo-oxidative stability of the Fortafil 5/PMR-15 composite relative to the excellent thermo-oxidative stability of the Fortafil 5(u) fiber itself suggests that the interface region in this system is the weak link and the point at which the composite system is thermo-oxidatively degraded. The higher weight loss of the AS4(u)/PMR-15 composite system relative to the neat AS4(u) fiber itself also suggests that interaction effects in the interface region of the composite may be responsible for this behavior. The relatively good agreement in weight losses of the Celion 6000 unsized and PI sized composites with weight losses of the neat fibers indicates that this interface region is not being degraded and, as mentioned above, that the exposed fiber is protecting the underlying composite system.

Optical Micrographs of Polished Cross Sections of Isothermally Aged Composites

In order to determine the extent of cracking in the composite due to isothermal aging, a shear specimen from each series was ground and polished. The total grinding and polishing depth required before any evidence of cracking was eliminated from each composite was determined.

Optical micrographs of the polished cross sections (Figs. 14-18) reveal that after grinding and polishing to a depth of 0.19 cm (0.075 in.), into the Celion 6000(u)/PMR-15 composite, a crack and void-free composite was found. Surface cracks which develop at the ends of the Celion 6000(u)/PMR-15 composite during aging do not penetrate the composite. In the other composites, after grinding to a depth of 1.1 cm (0.45 in.), each still showed the presence of at least one major flaw or crack and the presence of voids in the interface region of the composite. It should be noted that even though most of the composites contained one large flaw or crack area, the remainder of the composite was essentially free of voids and cracks. This is strong evidence that the PMR-15 polyimide resin matrix does not undergo thermo-oxidative or pyrolytic degradation in the internal regions of the composite. The major thermo-oxidative degradation process occurs on the external surface. The evidence for this is (1) the weight losses, (2) size reduction of cross sections (Figs. 14-18) of each composite, and (3) void-free regions in the matrix of the aged composites.

Mechanical Properties of Isothermally Exposed Composites

Elevated temperature flexural and shear strengths of these composite systems after aging at 350°C for several hours in flowing air are listed in Tables 10 and 11 respectively. The "as fabricated" properties are listed for comparison.

The higher flexural properties after aging at 350°C for 250 hrs is due to a postcure effect (ref. 7), which causes an improvement in the properties over the initial unaged composite. Inspection of Table 10 shows that only two composites retain a reasonable fraction of the unaged or 250 hr aged properties. These are the Celion 6000 unsized and PI sized fiber/composite systems. The behavior of these composites in shear (Table 11) is similar to that observed with the flexural properties. There is an improvement in the shear strength for most composite systems after 250 hrs exposure at 350°C, due to the postcure effect. However, only two composite systems retain a reasonable fraction of the unaged and 250 hr aged properties. These are the Celion 6000 unsized and PI sized composites, with the unsized fiber system displaying superior thermo-oxidative resistance relative to the PI sized Celion 6000 composite, and vastly superior oxidation resistance to the Thorne1 300(u), AS4(u), Fortafil 5(u) and Panex 30(u) composite systems. A comparison of the component and composite weight loss rates, the sodium content on fiber/composite systems and 350°C flexural strength after 520 hrs is listed in Table 12. The stability of the Celion 6000(u)/PMR-15 composite, and by inference, the apparent stability of the fiber-matrix interface region is clearly shown when the rate of oxidation of the fiber, resin and composite and the flexural strength of the aged composite are considered. The protective effect of the fiber on the surface of the composite is illustrated by the strength of the aged composite, and is further illustrated by the photomicrograph of the cross section (transverse to the fiber direction) of the Celion 6000(u)/PMR-15 composite (Fig. 14). The photomicrograph of a shear specimen 1.52 cm (0.6 in.) in length reveals that no degradation occurs at the interface, and that there is no apparent pyrolysis or thermo-oxidative degradation of the matrix in the bulk of the composite. Surface cracks which develop at the ends of the composite during aging do not penetrate the composite. This was illustrated by the observation that after grinding and polishing the aged composite to a depth of 0.19 cm (0.075 in.), all evidence of surface cracks was removed (Fig. 14). Micrographs of shear specimens of the other composites (Figs. 15-18) reveal the presence of at least one major flaw or crack through the entire composite and the presence of voids in the interface regions of the composites.

CONCLUSIONS

The surfaces of commercial graphite fibers contain sodium, potassium, calcium, chromium and iron in varying relative atomic ratios. For 350°C applications in flowing air (100 cc or 1000 cc/min), the fiber rating in PMR-15 composites is as follows: Celion 6000(u) > Celion 6000 (PI Celanese size) > Fortafil 5(u) > AS4(u) > Thorne1 300(u) > Panex 30(u). The thermo-oxidative stability of the above fibers in

the neat form and the PMR-15 resin under the same conditions is as follows: Fortafil 5(u) >> Celion 6000(u) > AS4(u) > Celion 6000 (PI Celanese size) > PMR-15 > Thorne1 300(u) > Panex 30(u). The greater thermo-oxidative stability of composites relative to the fiber and polyimide matrix can be attributed to an overall protective blanket provided by the fiber after the resin is oxidized. The formation of a passive layer on the matrix due to deposition of components from the fiber can also be the method by which thermo-oxidative process is retarded. The formation of these protective barriers appears to be the mechanism of degradation for composites which exhibit internal thermo-oxidative stability and no internal pyrolysis of the matrix, namely the Celion 6000(u) and Celion 6000 (PI)/PMR-15 systems. For composites which show good fiber thermo-oxidative stability, such as Fortafil 5(u) and AS4(u), two factors may be responsible for the poor thermo-oxidative stability of the composite and subsequent poor mechanical properties. The first is (1) the aging process may generate poor bonding at the fiber/matrix interface, and (2) impurity components on the fiber, such as sodium or potassium ions, may accelerate thermo-oxidation of the resin and fiber in the interface region. Those composite systems which exhibited the poorest thermo-oxidative stability contain substantial quantities of sodium and potassium on the fiber, relative to the more thermo-oxidatively stable composite systems.

The fiber degradation rate appears to have a significant influence on the thermo-oxidative stability of the PMR-15 composite. The major degradation process occurs via thermo-oxidation of the surface of the composite. There is no evidence of internal oxidation or pyrolysis of the polyimide matrix under these conditions.

REFERENCES

1. Scola, D. A.: A Study of the Thermo-oxidative Process and Stability of Graphite and Glass/PMR Polyimide Composite. SAMPE, 27th National SAMPE Symposium and Exhibition, San Diego, CA, Vol. 27, 923-939 (1982).
2. Gibbs, H. H.; Wendt, R. C.; and Wilson, F. C.: SPI, 33rd Annual Technical Conference, Reinforced Plastics/Composites Institute, Section 24-F (1978).
3. Drzal, L. T.; and Hammer, G. E.: ALWAL-TR-80-4143, April 1981.
4. Serafini, T. T.; Delvigs, P.; and Lightsey, G. R.: U.S. Patent 3,745,149, July 1973.
5. Serafini, T. T.; Delvigs, P.; and Lightsey, G.R.: J. Poly. Sci., Vol. 16, No. 4, pp 905-915 (1972).
6. DiBenedetto, A. T.; and Scola, D. A.: J. Colloid & Interface Science, Vol. 64, No. 3, pp 480-500 (1978).
7. Pater, R. H.: Novel Improved PMR Polyimides. 13th National SAMPE Technical Conference, 13, 38-52 (1981).

TABLE 1. - ISS/SIMS ANALYSIS

Conditions:

Energy of primary ion beam	2.5 keV
Beam current	40 nAmps
Current density	1.3 μ amps/cm ²
Rastered area	(1x3) mm ²
Gated area	70% of rastered area
Sputter rate	~2 \AA /min

Analysis:

ISS - First scan with ³He (2 scans, 3 minutes each) to detect scattered ³He⁺ ions only; sensitive to low atomic no. elements

SIMS- Second scan with ²⁰Ne (2 scans) to detect ⁺ and ⁻ secondary ions; sensitive to higher atomic no. elements and molecular fragments

TABLE 2. - SIMS ANALYSIS OF GRAPHITE FIBER SURFACES

Fiber	Relative Atomic Ratio -10 \AA ²⁰ Ne					
	Na	K	Ca	Cr	Fe	F
Panex 30(u)	110	1.0	-	7.9	23	-
Fortafil 5(u)	2.0	1.0	-	9.4	21	-
Celion 6000(u)	8.4	1.0	33	4.4	15	-
Thorne1 300(u)	3.1	1.0	1.7	-	18	-
AS4(u)	2.8	1.0	3.2	-	-	17
Celion 6000(PI)	3.5	1.0	20	-	15	-

TABLE 3. - SIMS ANALYSIS OF GRAPHITE FIBER SURFACES

Fiber	Relative Atomic Ratio ~100Å ²⁰ Ne					
	Na	K	Ca	Cr	Fe	F
Panex 30(u)	11	1.0	-	3.2	5.2	-
Fortafil 5(u)	1.6	1.0	-	5.1	3.7	-
Celion 6000(u)	2.2	1.0	5.3	4.8	6	-
Thorne1 300(u)	1.7	1.0	1.7	5.2	7.5	-
AS4(u)	6.0	2.6	3.2	2.7	5.3	1.0
Celion 6000(new PI)	2.0	1.0	1.4	2.4	5.1	-

TABLE 4. - SIMS ANALYSIS OF GRAPHITE FIBERS

Fiber	Relative Atomic Ratio (Counts/sec ¹) 10Å Ne					
	Na	K	Ca	Cr	Fe	F
Panex 30(u)	43	1.0	-	2.0	1.0	-
Fortafil 5(u)	1.0	1.3	-	3.2	1.3	-
Celion 6000(u)	5.2	1.6	18	1.8	1.1	-
T300(u)	1.9	1.6	1.0	-	1.4	-
AS4(u)	1.5	1.4	1.6	-	1.6	1.0
Celion 6000(PI)	1.5	3.8	1.3	1.0	-	-

¹ actual counts/sec for element in lowest count/sec

Fortafil 5(u)	Na 1348	Celion 6000(PI)	Cr 37
Panex 30(u)	K 475	Panex 30(u)	Fe 127
T300(u)	Ca 186	AS4(u)	F 492

TABLE 5. - SIMS ANALYSIS OF GRAPHITE FIBERS

Fiber	Relative Atomic Ratio (Counts/sec ¹) 100Å Ne					
	Na	K	Ca	Cr	Fe	F
Panex 30(u)	28.0	6.1	-	1.7	2.0	-
Fortafil 5(u)	2.5	3.9	-	1.7	1.1	-
Celion 6000(u)	2.2	2.4	2.4	1.0	1.1	-
T300(u)	2.1	3.2	1.0	1.3	1.3	-
AS4(u)	71	75	18	6.5	9.2	-
Celion 6000(PI)	1.0	1.0	4.6	-	1.0	1.0

¹ actual counts/sec for element in lowest count/sec

Celion 6000(PI)	Na 1814	Celion 6000(u)	Cr 161
Celion 6000(PI)	K 670	Celion 6000(PI)	Fe 127
T300(u)	Ca 500	Celion 6000(PI)	F 866

TABLE 6. - SIMS ANALYSIS OF GRAPHITE FIBER/PMR-15 COMPOSITES
AFTER 250 HRS AT 350°C, 1000 CC/MIN (AIRFLOW)

Fiber	Relative Atomic Ratio (Counts/sec ¹) 10Å Ne					
	Na	K	Ca	Cr	Fe	F
Panex 30(u)	9.5	5.4	1.0	4.4	1.0	-
Fortafil 5(u)	5.4	10	11	1.0	29	1.7
Celion 6000(u)	1.0	1.9	18	8.0	17	1.0
Thornel 300(u)	4.2	1.0	2.4	3.4	33	-
AS4(u)	3.5	2.0	6.3	3.1	59	1.1
Celion 6000 (Celanese PI size)	1.0	4.0	17	16	127	-

¹ actual counts/sec for element in lowest count/sec from fiber to fiber

Celion 6000(PI)	Na 21,958	Fortafil 5(u)	Cr 25
T300(u)	K 4,076	Panex 30(u)	Fe 51
Panex 30(u)	Ca 37.3	Celion 6000(u)	F 652

TABLE 7. - SIMS ANALYSIS OF GRAPHITE FIBER/PMR-15 COMPOSITES
AFTER 250 HRS AT 350°C, 1000 CC/MIN (AIRFLOW)

Fiber	Relative Atomic Ratio (counts/sec ¹)					
	100Å Ne					
	Na	K	Ca	Cr	Fe	F
Panex 30(u)	30	1.1	1.0	1.0	1.0	-
Fortafil 5(u)	8.8	6.6	26	3.1	13	3.3
Celion 6000(u)	1.0	1.0	30	5.4	19	1.0
Thorne1 300(u)	10	1.1	11	5.0	15	-
AS4(u)	5.4	1.6	14	4.7	12	7.6
Celion 6000 (Celanese PI size)	1.5	2.7	29	9.7	24	-

¹ actual counts/sec for element in lowest counts/sec from fiber to fiber

Celion 6000(u)	Na 4839	Panex 30(u)	Cr 25
Celion 6000(u)	K 1686	Panex 30(u)	Fe 25
Panex 30(u)	Ca 152	Celion 6000(u)	F 136

TABLE 8. - SIMS ANALYSIS OF FIBERS AND AGED COMPOSITES FOR SODIUM

Fiber/PMR-15 Composite	Relative Atomic Ratio (Counts/sec ¹)			
	Fiber		Composites 250 hrs at 350°C 1000 cc/min (airflow)	
	10Å	100Å	10Å	100Å
Celion 6000(u)	5.2	2.2	1.02	1.0
Celion 6000(PI)	1.5	1.0	1.0	1.5
Thorne1 300(u)	1.9	2.1	4.2	10
AS4(u)	1.5	71	3.5	5.5
Fortafil 5(u)	1.0	2.5	5.4	8.8
Panex 30(u)	43	28	9.5	30

¹ See Tables 4, 5, 6, and 7 for actual counts/sec

TABLE 9. - COMPONENT AND COMPOSITE WEIGHT LOSSES AT 350°C
(1000 cc/min airflow)

Fiber/PMR-15 Composite	Fiber ¹ Wt% Loss after 450 hrs	Composite Wt% Loss after 520 hrs
Celion 6000(u)	11.2	12.5
Celion 6000(PI)	16.0	12.0
Thorne1 300(u)	94.2	40.0
AS4(u)	10.4	21.1
Fortafil 5(u)	0.43	24.3
Panex 30(u)	99.5	95
PMR-15 resin ¹	77.8 ¹	-

¹PMR-15 resin is listed in this column (after 385 hrs)

TABLE 10. - FLEXURAL PROPERTIES OF ISOTHERMALLY AGED PMR-15 COMPOSITES
(350°C, 1000 cc/min airflow)

Composite System	350°C Flexural Properties					
	Unaged		After 250 hrs		After 520 hrs	
	Strength MPa (ksi)	Modulus GPa (10 ⁶ psi)	Strength MPa (ksi)	Modulus GPa (10 ⁶ psi)	Strength MPa (ksi)	Modulus GPa (10 ⁶ psi)
Celion 6000(u)	269 (39)	49.7 (7.2)	373 (54)	58.7 (8.5)	421 (61)	87.6 (12.7)
Thorne1 T300(u)	366 (53)	42.8 (6.2)	366 (53)	96.6 (14)	82.8 (12)	11.0 (1.6)
Celion 6000(PI)	276 (40)	39.3 (5.7)	656 (95)	159 (23)	297 (43)	60.7 (8.8)
AS4(u)	297 (43)	46.9 (6.8)	469 (68)	145 (21)	124 (18)	65.5 (3.7)
Fortafil 5(u)	379 (55)	48.9 (7.1)	814 (118)	138 (20)	221 (32)	82.8 (12)
Panex 30(u)	393 (57)	69.0 (10)	173 (25)	19.3 (2.8)	completely degraded	-

TABLE 11. - INTERLAMINAR SHORT BEAM SHEAR STRENGTH OF
ISOTHERMALLY AGED PRM-15 COMPOSITES
(350°C, 1000 cc/min airflow)

Composite System	350°C Shear Strength, MPa (ksi)		
	Unaged	After 250 hrs	After 520 hrs
Celion 6000(u)	19.3 (2.8)	34.3 (4.97)	33.1 (4.8)
Thorne1 300(u)	28.9 (4.2)	28.3 (4.10)	6.76 (0.98)
Celion 6000(PI)	26.9 (3.9)	29.7 (4.3)	13.4 (1.94)
AS4(u)	12.4 (1.8)	23.8 (3.45)	2.85 (0.413)
Fortafil 5(u)	13.1 (1.9)	23.5 (3.40)	4.41 (0.64)
Panex 30(u)	20.0 (2.9)	mostly fiber remaining	mostly fiber remaining

TABLE 12. - COMPARISON OF COMPONENT AND COMPOSITE PROPERTIES
(after 350°C, 1000 cc/min airflow)
520 hrs

Fiber/Composite Systems	Fiber Wt Loss Rate 10 ⁻⁴ g/hr	Composite Wt Loss Rate 10 ⁻⁴ g/hr	Fiber Composite Sodium Content Rel. Atomic Ratio ¹ ~100Å	350°C Flexural Strength ksi
Celion 6000(u)	11.0	3.1	1.0	61
Celion 6000(PI)	15.5	3.7	1.5	43
Fortafil 5(u)	0.40	3.9	8.8	32
AS4(u)	11.0	5.4	5.5	18
Thorne1 300(u)	86	10.9	10	12
Panex 30(u)	140	25	30	completely degraded
PMR-15 resin	5.7	-	-	

¹ where 1.0 = 4839 counts/sec of sodium

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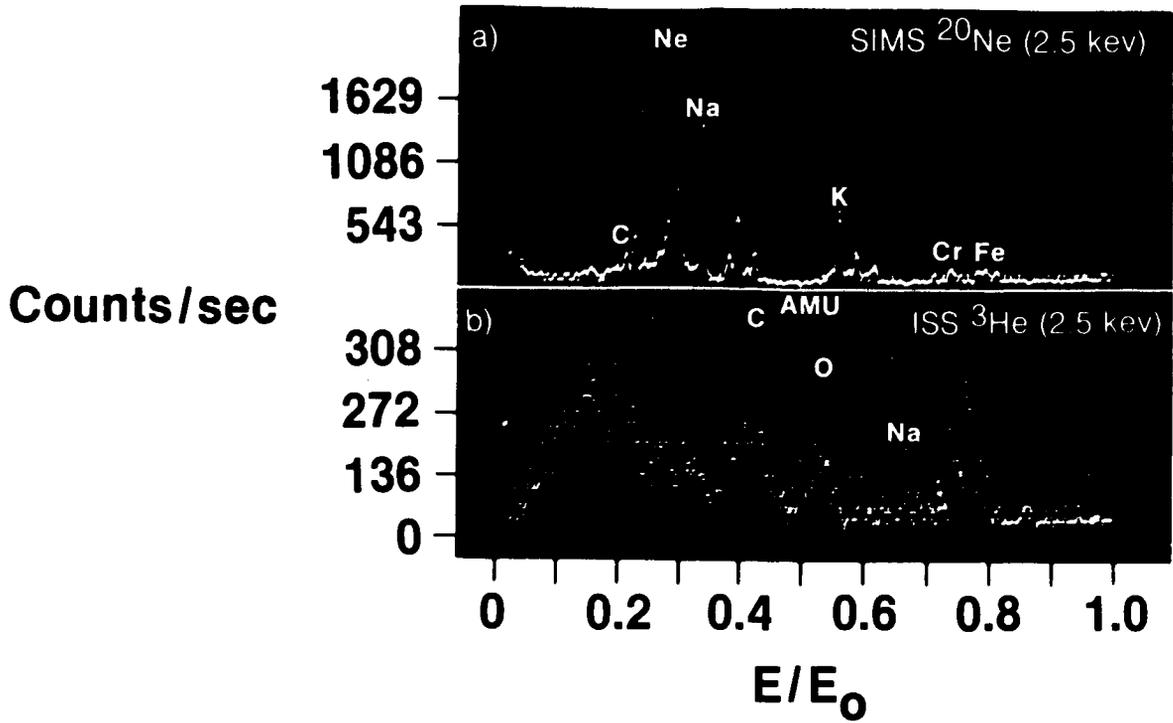


Figure 1. - ISS/SIMS spectra of Fortaf11 5 unsized fiber $\sim 10\text{\AA}$.

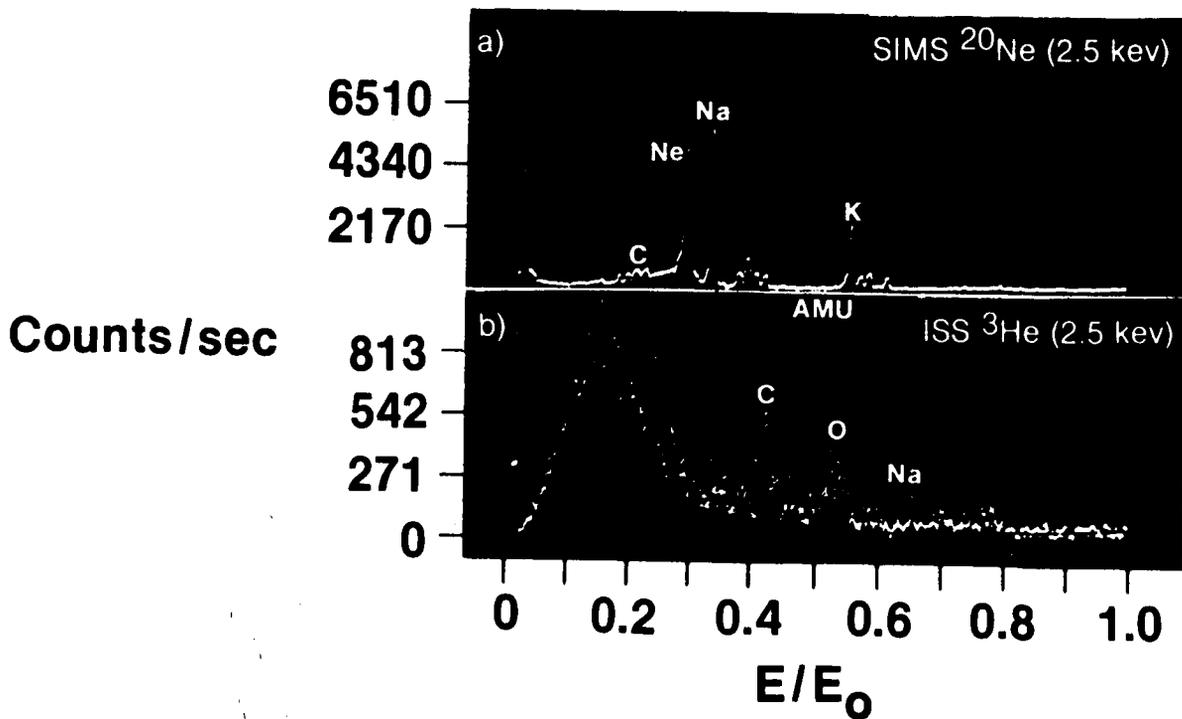


Figure 2. - ISS/SIMS spectra of Fortaf11 5 sized fiber $\sim 10\text{\AA}$.

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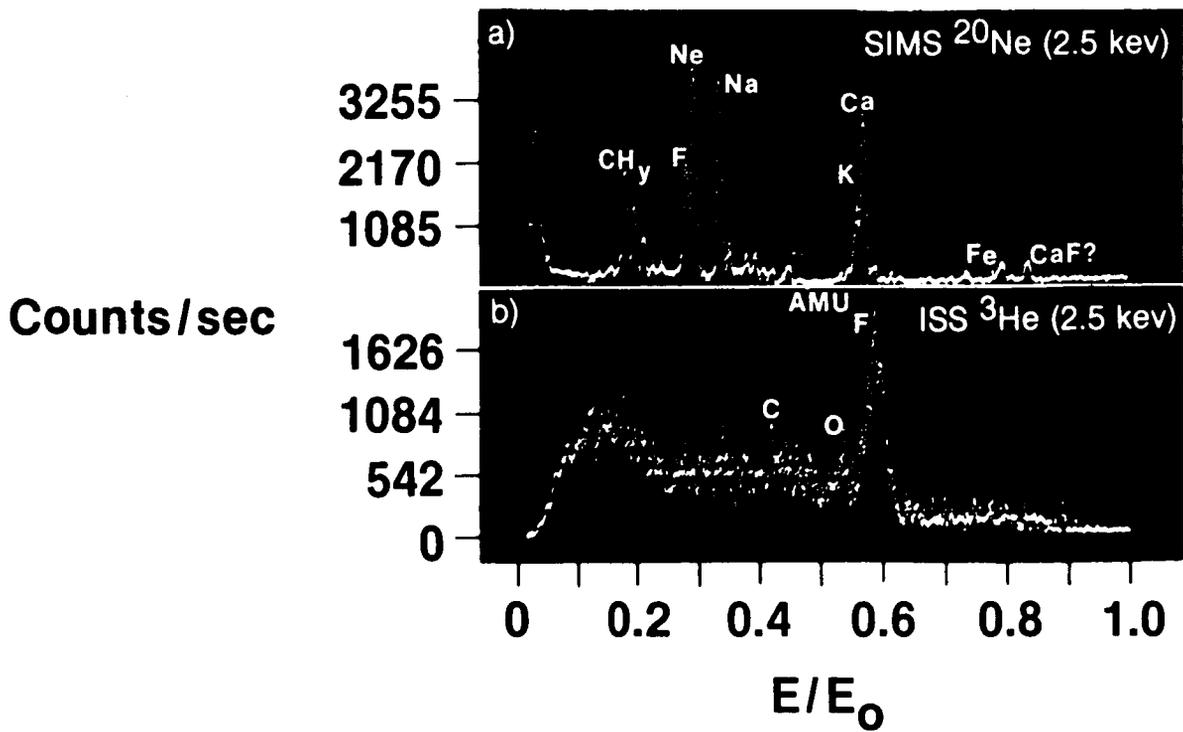


Figure 3. - ISS/SIMS spectra of Celion 6000 NR150B2 sized fiber $\sim 10\text{\AA}$.

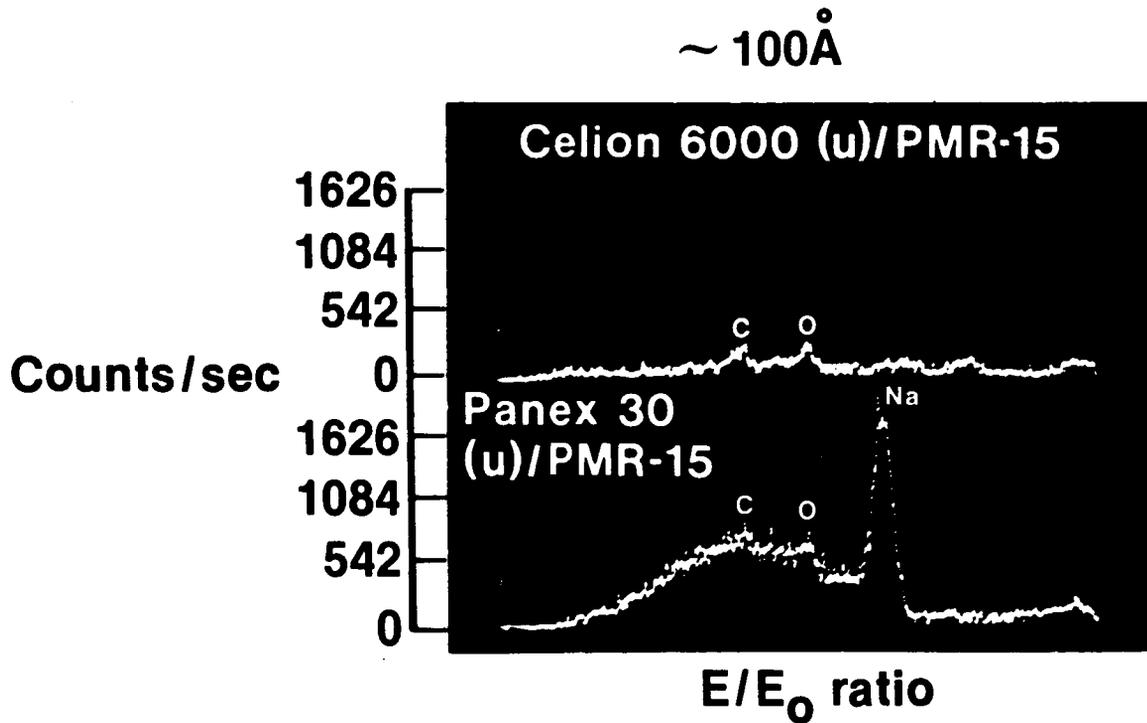


Figure 4. - ISS spectra of isothermally aged composites.
(350 °C, 220 hrs, 1000 cc/min airflow)

~ 10Å

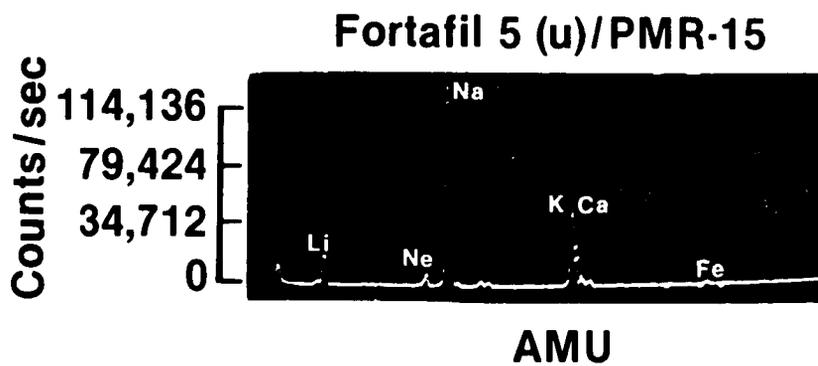
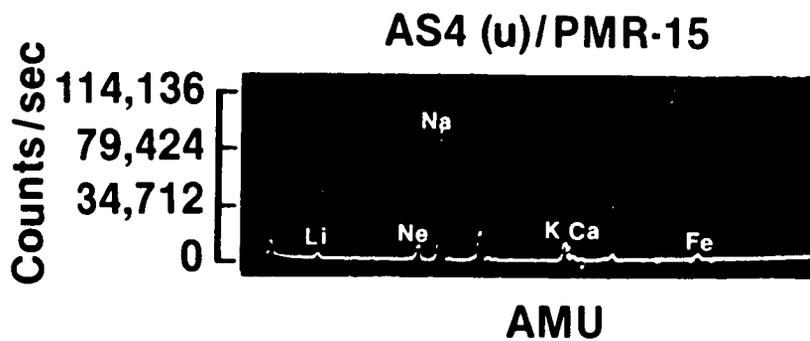
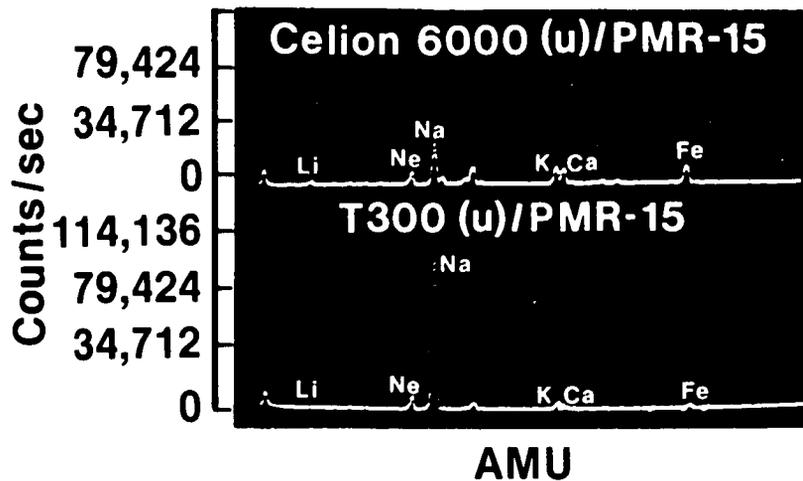
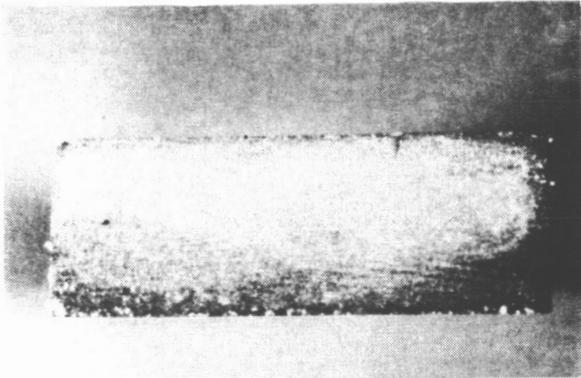
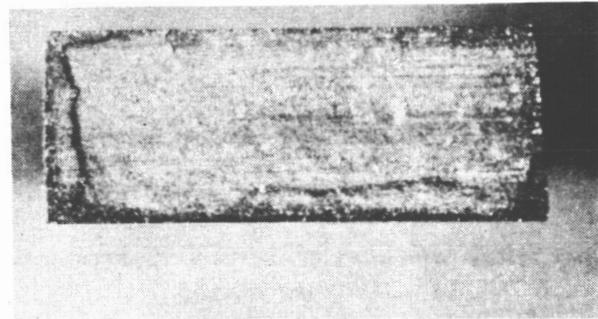


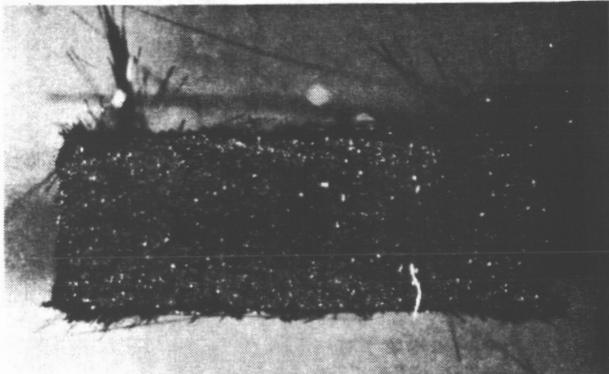
Figure 5. - SIMS spectra of isothermally aged composites.
(350 °C, 220 hrs, 1000 cc/min airflow)



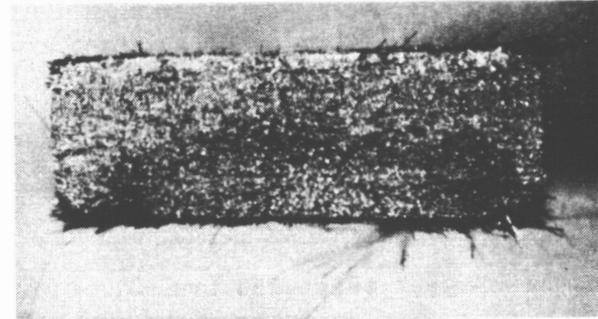
6a. As fabricated



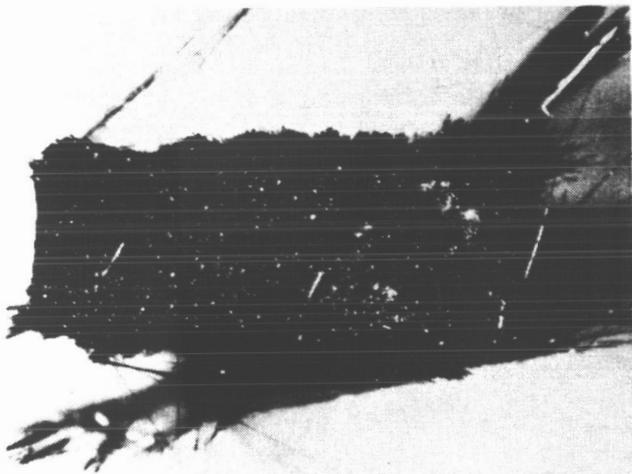
7a. As fabricated



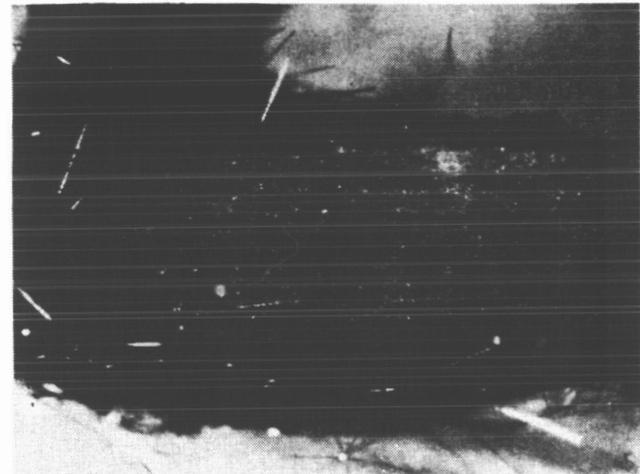
6b. After 250 hrs



7b. After 250 hrs



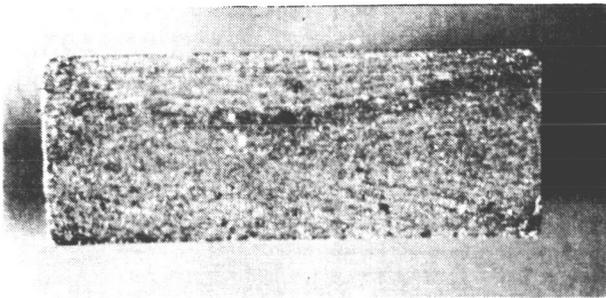
6c. After 520 hrs



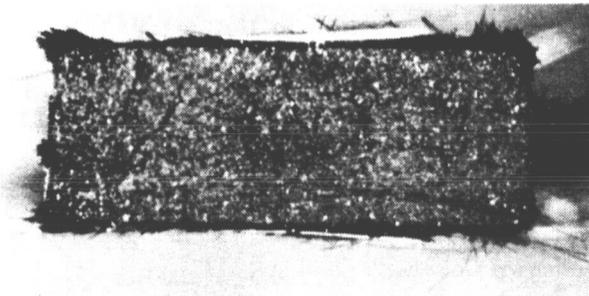
7c. After 520 hrs

Figure 6. - Thermo-oxidation process of
graphite fiber/PMR-15 composites.
(350 °C, 1000 cc/min airflow)
Celion 6000 (u)/PMR-15

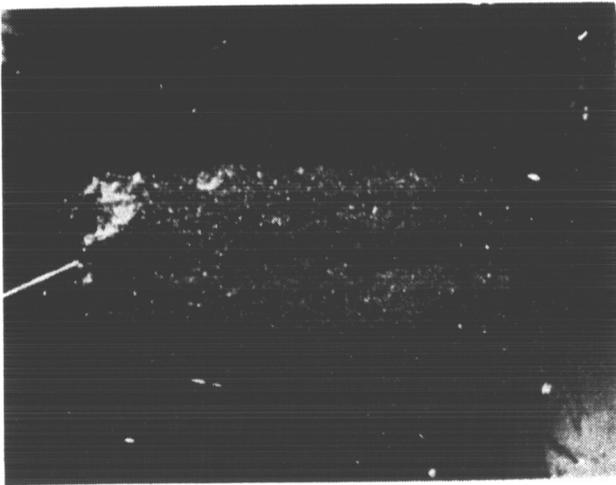
Figure 7. - Thermo-oxidation process of
graphite fiber/PMR-15 composites.
(350 °C, 1000 cc/min airflow)
Celion 6000 (PI sized)/PMR-15



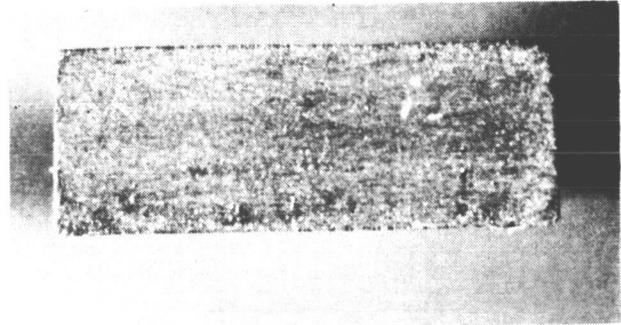
8a. As fabricated



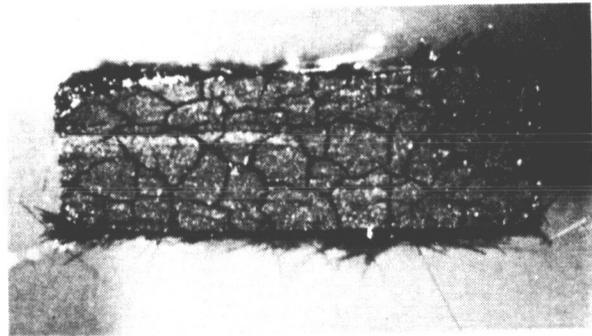
8b. After 250 hrs



8c. After 520 hrs



9a. As fabricated



9b. After 250 hrs



9c. After 520 hrs

Figure 8. - Thermo-oxidation process of graphite fiber/PMR-15 composites.

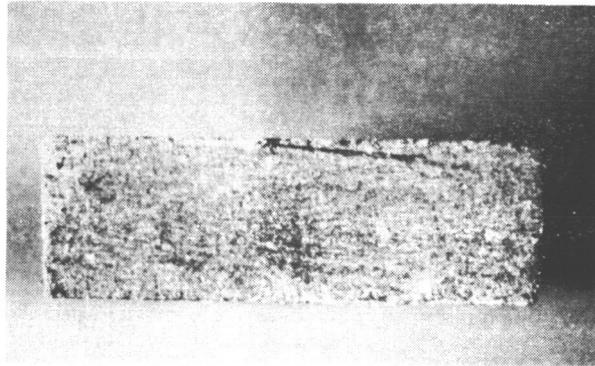
(350 °C, 1000 cc/min airflow)

AS4 (u)/PMR-15

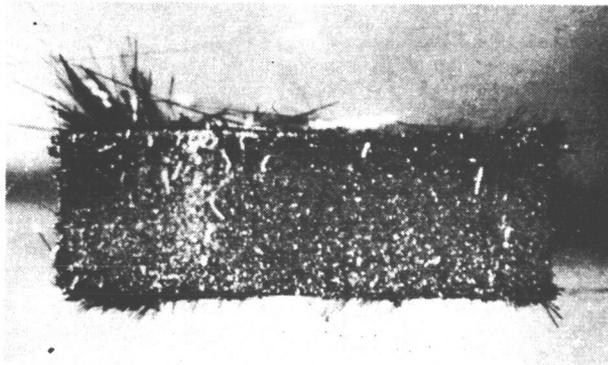
Figure 9. - Thermo-oxidation process of graphite fiber/PMR-15 composites.

(350 °C, 1000 cc/min airflow)

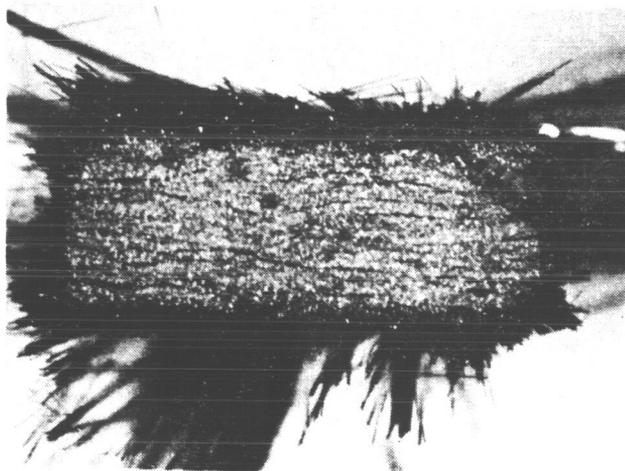
Thorne1 300 (u)/PMR-15



10a. As fabricated



10b. After 250 hrs

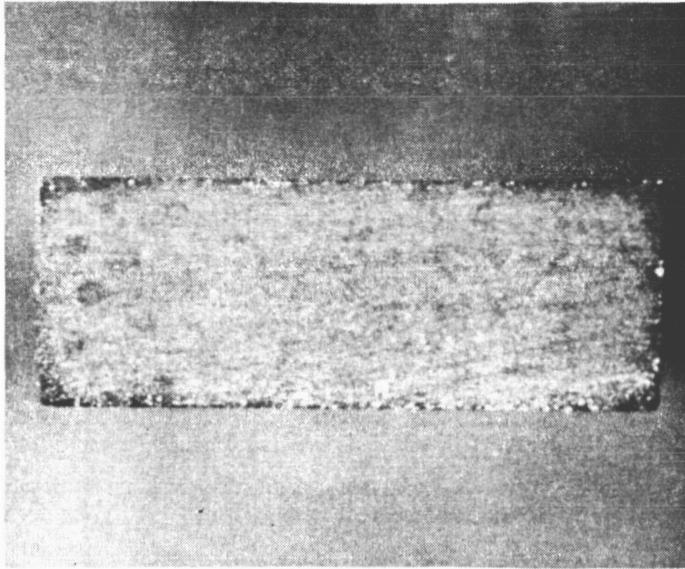


10c. After 520 hrs

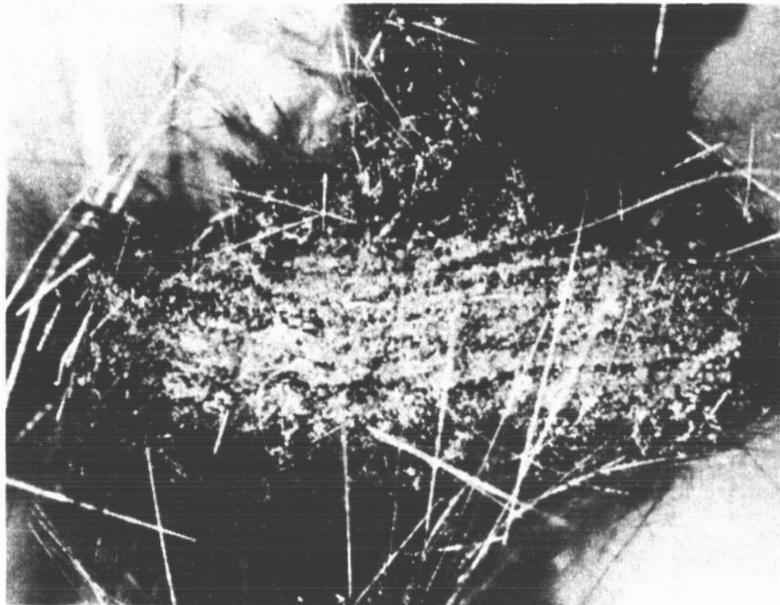
Figure 10. - Thermo-oxidation process of
graphite fiber/PMR-15 composites.

(350 °C, 1000 cc/min airflow)

Fortafil 5 (u)/PMR-15



11a. As fabricated



11b. After 250 hrs

Figure 11. - Thermo-oxidation process of graphite
fiber/PMR-15 composites.

(350 °C, 1000 cc/min airflow)

Panex 30 (u)/PMR-15

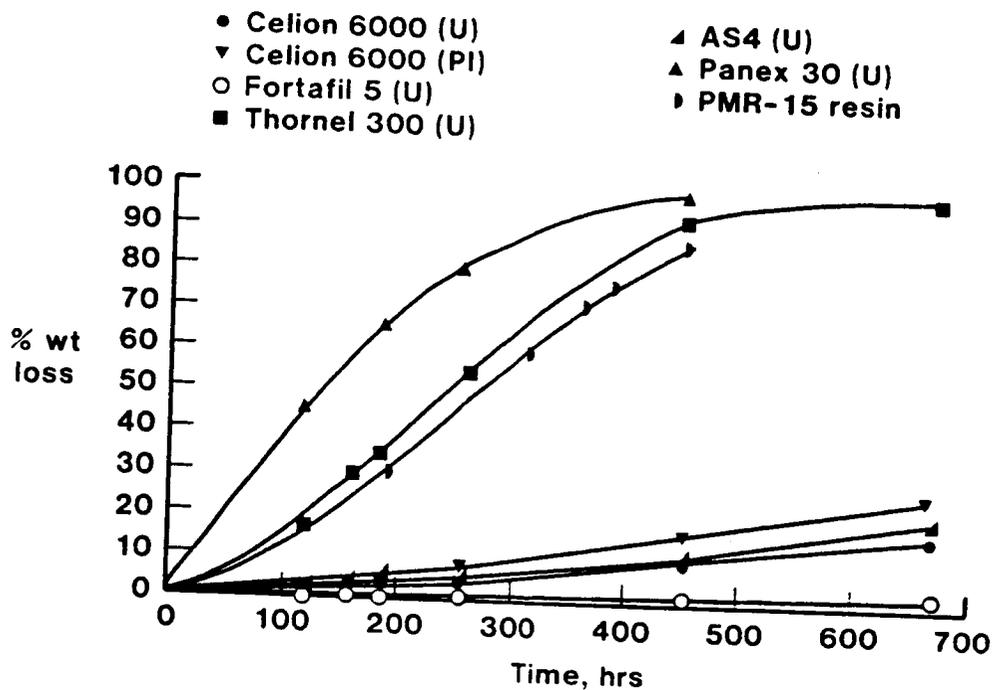


Figure 12. - Weight loss of component materials.
(350 °C, 1000 cc/min airflow)

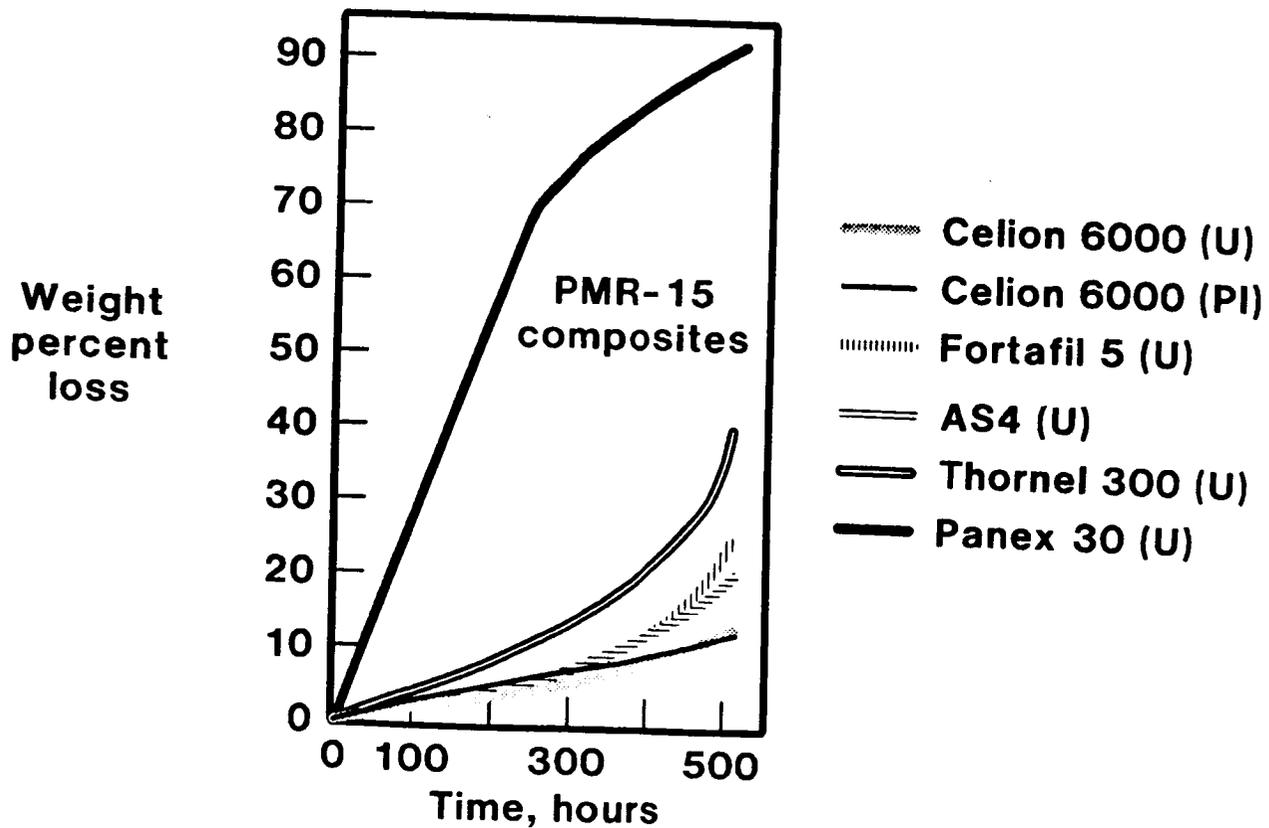
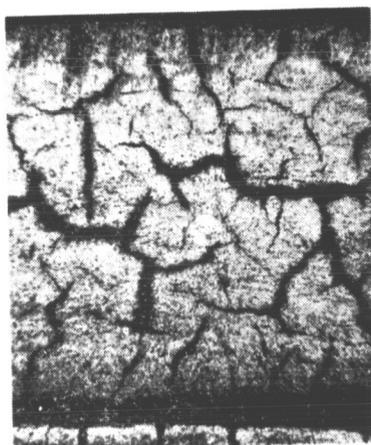


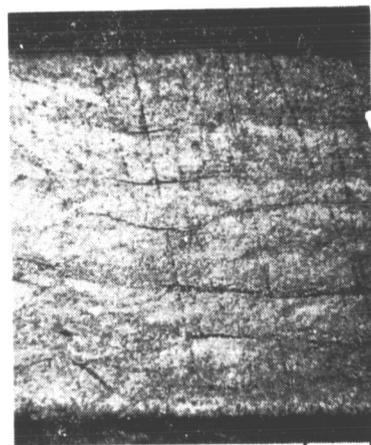
Figure 13. - Composite weight loss.
(350 °C, 1000 cc/min airflow)



14a. As fabricated



14b. After 250 hrs



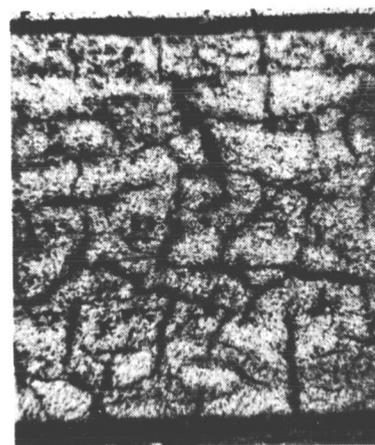
400 μ m

14c. After polishing 0.075 in.
(depth of crack)

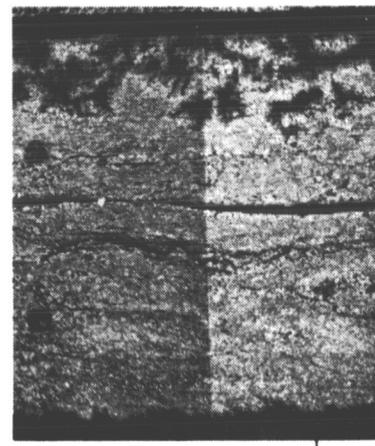
Figure 14. - Cross section of Celion 6000 (u)/PMR-15 composite.
(350 °C, 1000 cc/min airflow)



15a. As fabricated



15b. After 250 hrs



400 μ m

15c. After polishing 0.45 in.

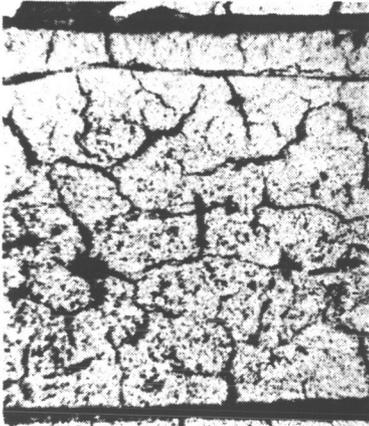
Figure 15. - Cross section of Celion 6000 (PI)/PMR-15 composite.



16a. As fabricated



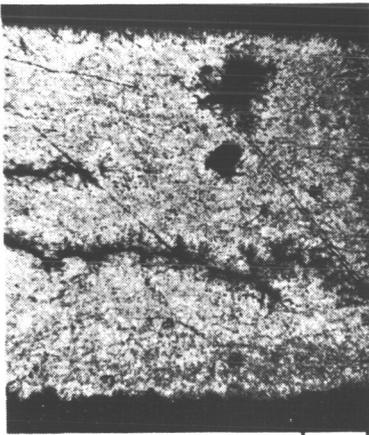
17a. As fabricated



16b. After 250 hrs

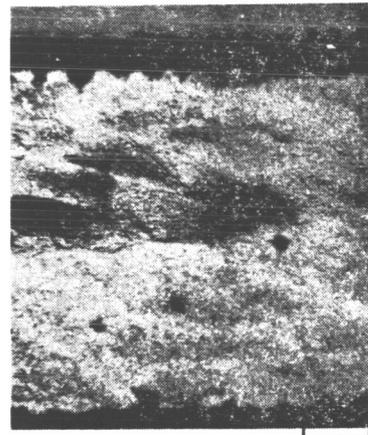


17b. After 250 hrs



400 μ m

16c. After polishing 0.45 in.



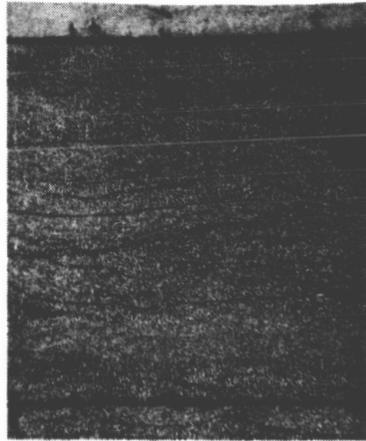
400 μ m

17c. After polishing 0.45 in.

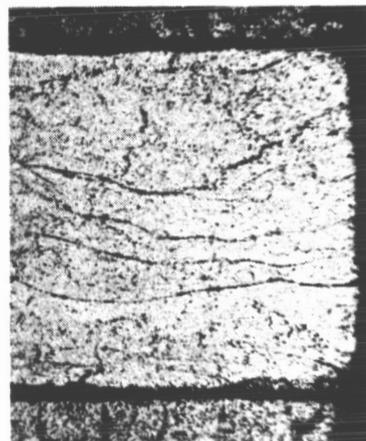
Figure 16. - Cross section of AS4
(u)/PMR-15 composite.
(350 °C, 1000 cc/min airflow)

Figure 17. - Cross section of Thorne1
300 (u)/PMR-15 composite.
(350 °C, 1000 cc/min airflow)

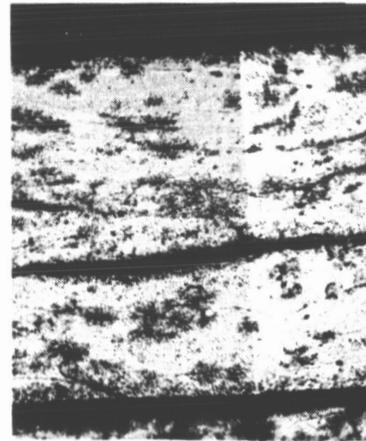
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18a. As fabricated



18b. After 250 hrs



400 μ m

18c. After polishing 0.45 in.

Figure 18. - Cross section of Fortafil 5
(u)/PMR-15 composite.